

TVA/EPRI/DOE 1998 Cumberland Plume Study

Progress Report

Prepared by

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Introduction

Because SO₂ emissions reductions have reduced sulfate aerosol formation in scrubbed power plant plumes, for example, the CUF fossil plant at Cumberland City, TN, primary sulfate emissions may now be comparable in mass and volume to secondary sulfate aerosol formation within the identifiable plume. As well, secondary nitrate particles may be important contributors to fine particulate mass in scrubbed plumes with comparatively high NO_x emissions. Data has been collected during the 1998 portion of the Cumberland Visible Emissions Study on the changes (and rates of changes where possible) in total mass, size distributions, and chemical composition of in-plume fine particles. This data will be used to evaluate emerging EPRI and EPA plume particle models. Additional data on concentrations of gaseous species in the CUF plume were also collected which will refine our knowledge of what factors most influence the fate of plume NO_x, determine the efficiency of ozone formation in the plumes of large stationary sources, and help understand how that efficiency may change with the installation of NO_x control technology. Another objective of this project is to identify the potential for changes in primary and secondary PM_{2.5} emissions from further NO_x reductions at large power plants. To summarize, this study has examined emissions and in-plume processes from a coal-fired unit (Cumberland) before and, in 1999, will examine emissions and in-plume processes after the installation of low-NO_x burners on one of the two CUF units, to determine if the modification has significantly affected the primary emissions or secondary gaseous and particle formation processes.

Experimental

A study of plume chemistry using an instrumented helicopter was conducted in the summer of 1998 to address fine particle formation and the relative contributions of primary sulfate and secondary nitrate and sulfate to fine particulate mass. Funding for the project was provided by TVA, DOE and EPRI. Eight plume sampling flights were conducted in August, 1998, with a break between the first four and the last four flights. In general, the meteorological conditions were not favorable for sampling the CUF plume in isolation from other power plants during the study. Flight 8 on August 25 is considered the best flight based on instrument performance and plume isolation. At the furthest crosswind distance, there may have been some overlap with the plume of the Johnsonville fossil plant (JOF) at the southernmost portion of the traverse even on this day. In the plots given below, data from Flight 8 are used for illustration.

MANUFACTURER AND MODEL	PARAMETER	RANGE												
Particle Measuring Systems model PCASP particle size instrument	number of particles per optical particle size bin*	0.09 - 3.0 microns												
3-wavelength Nephelometer, TSI Model 3550	light scattering of blue, green and red λ	0.1 - 100 $\times 10^{-4} \text{ m}^{-1}$												
Filter Sampler*	Sulfate, nitrate, H^+ and ammonium in particles	1 - 200 nmole/m ³												
Thermo Electron Model 42C Nitrogen Oxides Analyzer	NO_y ($\text{NO} + \text{NO}_2 + \text{other odd nitrogen species}$) gas concentration	Two ranges: 0.5 - 10 ppm (near-plume) & 0-0.5 ppm (far plume & bkgd.)												
Thermo Electron Model 42C Nitrogen Oxides Analyzer	NO_y^* ($\text{NO}_y - (\text{Nitric Acid} + \text{particulate nitrate})$)	Two ranges: 0.5 - 10 ppm (near-plume) & 0-0.5 ppm (far plume & bkgd.)												
Thermo Electron Model 42S Nitrogen Oxides Analyzer with upstream photolytic cell	NO_2 gas concentration	0 - 200 ppb												
Thermo Electron Model 42S Nitrogen Oxides Analyzer.	NO gas concentration	0 - 200 ppb												
Thermo Electron Model 42S Nitrogen Oxides Analyzer modified for fast response O_3 measurement	O_3 gas concentration	0 - 200 ppb												
Thermo Electron Model 43C Sulfur Dioxide Analyzer.	SO_2 gas concentration	0 - 1000 ppb												
Licor Model X	CO_2 gas concentration	0-500 ppm												
Apollo Loran-C and GPS systems	Latitude and Longitude of helicopter	+/- 100 meters												
	Temperature and Relative Humidity	0-50 °C and 0-100 %RH, respectively												
Thermo Environmental Instruments, Inc. Multigas Calibration System, Model 146.	calibration gases for O_3 , NO_2 , and NO .	<table> <tr> <td><u>GAS</u></td> <td><u>SPAN</u></td> <td><u>CONC</u></td> </tr> <tr> <td>O_3</td> <td>120</td> <td>ppb</td> </tr> <tr> <td>NO_2</td> <td>120</td> <td>ppb</td> </tr> <tr> <td>NO</td> <td>7.3</td> <td>ppm</td> </tr> </table>	<u>GAS</u>	<u>SPAN</u>	<u>CONC</u>	O_3	120	ppb	NO_2	120	ppb	NO	7.3	ppm
<u>GAS</u>	<u>SPAN</u>	<u>CONC</u>												
O_3	120	ppb												
NO_2	120	ppb												
NO	7.3	ppm												

*Integrative sampler with no recordable electronic outputs.

Table 1. Measurement and Calibration systems.

In Figure 1, we show a updated summary of the data status by flight for the critical parameters needed to meet the objectives of the study. We see that for the first few flights (Flights 1, 2, 3, and 5; Flt. 4 was a brief systems test flight), instrumental problems prevented the acquisition of some critical chemical/physical parameters needed.

- ◆ Nephelometer data is flagged as yellow due to cabin-air heating of the instrument (and incoming air) to significantly higher temperatures than outdoor air. For later flights, the instrument was moved outside to the right strut and the overheating problem was eliminated.

- ◆ The HiVol air system was not valved during the first 3 flights; operation of valves during later flights, activated when the HiVols were turned on, prevented passive sampling of any particles.

- ◆ An unstable baseline problem with a new NO_y instrument (TEII Model 42C) occurred during early flights despite extensive pre-study testing and calibration. Switching the NO_y and NO_y^* instruments isolated the problem to the instrument. Fast-time-response observations during a downward spiral in Flt. 6 identified the problem as a light leak which was found to be caused by defective shielding of the ozone reactant line to the 43C's cell by the manufacturer. Repair of the defective part eliminated the problem, but the result was no valid NO_y data for Flights 1-3, no valid NO_y^* data for Flights 5 & 6, and no valid nitrate data for Flights 1-6.

- ◆ NO_2 is flagged yellow pending some additional lab tests of the validity of the algorithm used for calculation.

- ◆ CO_2 data are not available for flights 1-5, and is flagged yellow for Flights 7-9. The instrument was operating but was subject to some baseline excursions of unknown origin. The data appear to be valid for parts of Flights 7-9, although the CUF plume is only detectable above background in traverses close to the plant (\leq about 20 nautical miles, nm).

- ◆ All other flags should be self-evident from the Figure.

Results and Discussion

Results from Particle Measurements. The two principal foci of the 1998 study were particle formation and growth, and ozone formation/fate of NO_x . Particle measurements were made continuously as follows: size/volume distributions by the PCASP optical particle counting system (15 bins), and particle light scattering at three λ by nephelometry. Chemical composition determinations were made of in-plume and background aerosol samples collected on a quartz filter by a HiVol sampling system. Sample sizes of $>5 \text{ m}^3$ were collected if sampling times exceeded about 12 min. Soluble sulfate and nitrate were determined by ion chromatography, and ammonium by automated colorimetry.

A comparison of the nephelometer-measured light scattering with scattering calculated from PCASP number distributions of particles is shown in Figure 2. The agreement is excellent and demonstrate that PCASP and nephelometer data are comparable with a few seconds time resolution. In Figure 3 are shown cumulative scattering

A Preliminary Look at the Cumberland 1998 Plume Study
REI 9/14/98, Rev RLT 3/23/99

		Flight								
			1-Aug	3-Aug	4-Aug	6-Aug	23-Aug	24-Aug	25-Aug	26-Aug
		Criticality	1	2	3	5	6	7	8	9
Helicopter Instrument Performance	Nephelometer	1								
	PMS	1								
	HiVol	1								
	O ₃	1								
	NO _y	1								
	NO _y *	1								
	NO ₂	1 [#]								
	SO ₂	1								
	CO ₂	3								
	Hydrocarbons	1								
	Relative Humidity	2								
	Temperature	2								
	Pressure	1								
	GPS	1								
	Pre and post flight multipoint calibrations	1								
Quality Assurance	Preflight Checklist	1								
	Inflight zero/span	1								
	Audit	3								
Data Recovery	Pressure Corrections	1								
	Fast	1								
	Slow	1								
	GPS	1								
Flight Conditions	PMS	1								
	Wind Direction*	1								
	Wind Speed	1								
Weather Data	Rain	1								
	Profiler In-Flight	2								
	Profiler Archive	1								
Data Analysis & Modeling Support	Weather Brief	1								
	ROME model runs	3								
	Same-day reporting	2								

NO₂ is listed as yellow pending additional lab tests of the validity of the algorithm used for calculation.

+ Refers to availability of current wind data from the profiler prior to takeoff and during flight.

Figure 1. Status of helicopter systems and procedures during the study.

Figure 2.

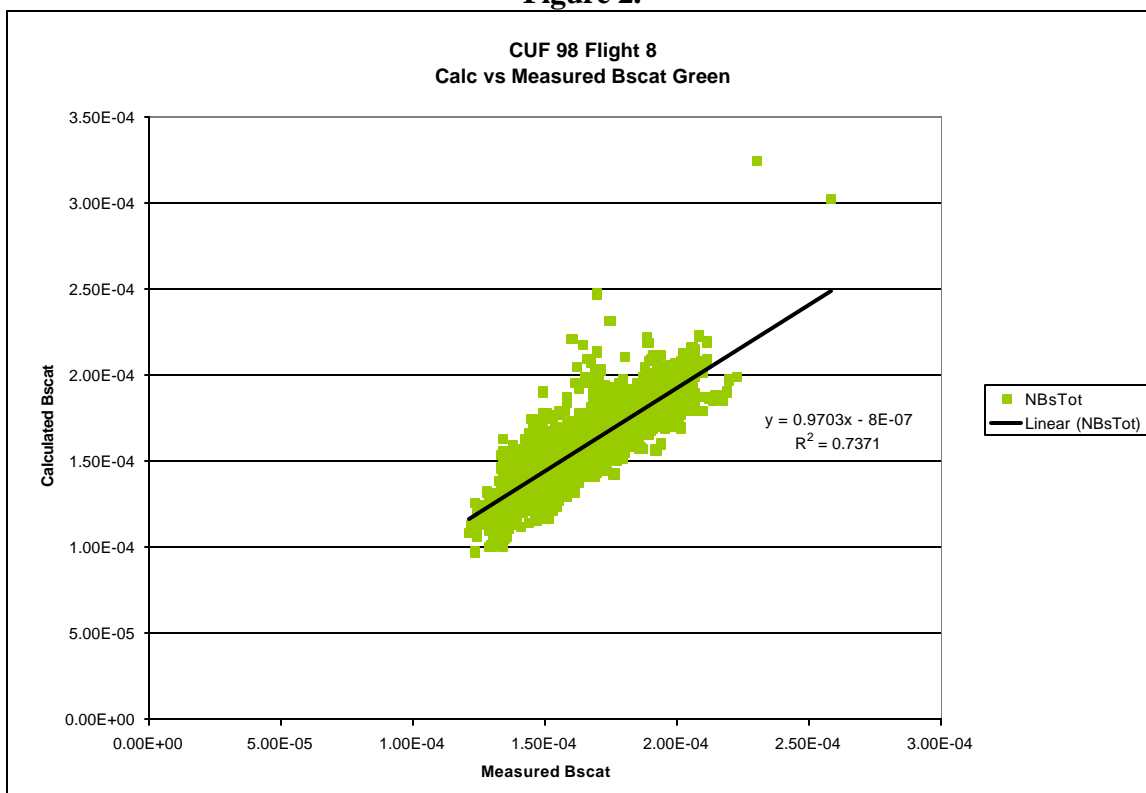


Figure 3. Cumulative Calculated Light Scattering (from PCASP Data) vs. Particle Size, Flight 8

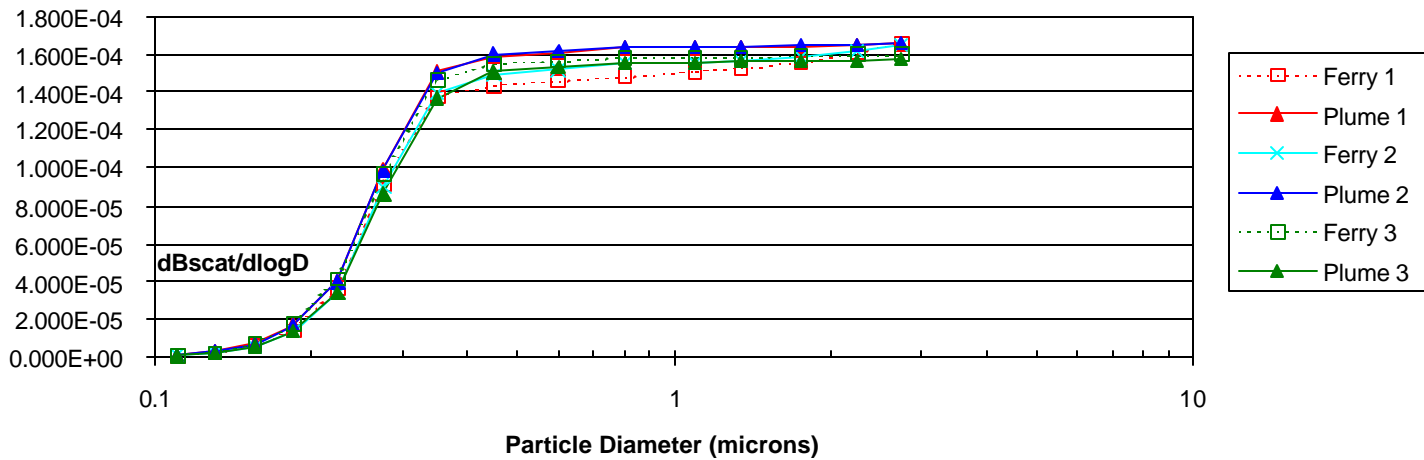


Figure 1. Cumulative light scattering vs. particle diameter for 6 sections of the flight. Ferries are the part of the flight going to a plume traverse distance, Plume is the integrated cross plume data. The distances sampled are (1) 10 nm, (2) 30 nm, and (3) 60 nm. Most of the light scattering has occurred by the particle diameter of 0.3 microns.

plots based on PCASP data from several plume traverses and ferries (in background air between plume penetrations) from flight 9. Most of the scattering is due to particles less than 0.5 μm on these flight segments. Relative contributions to scattering from particles in the 0.5-1.0 μm size range are larger in background air (encountered during “Ferries” between plume traverses) than in the plume, consistent with our knowledge of the size-fractionated emissions from the scrubbed CUF units.

The particle volume and light scattering can be used to identify the presence of the plume, as shown in Figure 4 in which volume and scattering are plotted vs. NO_y , our best indicated of the plume. The volume and scattering do go up in the plume during this traverse at 60 nm from the stack, but the change is small compared to background aerosol particle volume and scattering. The relationship between scattering and NO_y gives a better fit than P_{vol} vs. NO_y , probably because of limitations to the assumptions used in calculating particle volume from the PCASP particle count data.

In Figure 5 is shown both gaseous and aerosol data for a representative cross-plume traverse (Plume 9) at 60 nm during Flight 8, 8/25/98. The plume is most clearly seen in the NO_y trace, clearly seen for the nitrate ($\text{NO}_y\text{-NO}_y^*$) trace, and barely seen at this distance in the SO_2 trace, even with the greatly improved TEII Model 43C instrument being used. We can make out the plume from the 3- λ nephelometer, but with reduced differences relative to background going in order from the blue scattering signal to the green and then to the red signal. This is consistent with data described above in which most of the scattering from in-plume particles is due to those at the small end of the accumulation mode size range, thus one would expect greater plume differential scattering at the lower, blue wavelength, and least at the red wavelength. In contrast, the plume cannot be distinguished from the variability of the background using the total aerosol volume data derived from the PCASP system, at least in traverses at this distance. Using particle counts in the 0.1 to 0.3 μm range, however, the plume is clearly distinguishable although it does not contribute significantly to the total aerosol volume.

Finally, we present in Table 2 the chemical composition data for the HiVol samples from Flights 6-9. Data which are suspicious are shaded in the table, and are generally limited to samples of less than about 5 m^3 . In general, the data are consistent with a background aerosol whose sulfate concentrations are large compared to those nitrate, and in which the sulfate is about 50-80% neutralized (ammonium to sulfate molar ratios 1.0-1.6). There is some indication that the in-plume samples are (at least at the close in distances) more acidic than background, and that sulfate concentrations may increase (potentially due to in-plume reactions) further out in the plume. However, due to the wind direction-induced problems in sampling CUF when it was isolated from other plumes, it was not possible to sample at large enough distances from the plume to get clear-cut evidence of in-plume reactions to form secondary sulfate. This will be one of the principal goals of 1999 flights is to obtain this evidence of secondary sulfate formation if possible.



TenSPED version 2.2

Figure 4. Neph b_{sp} vs. NO_y Data for TVA
Julian Day: 237 1998 (8/25/98) Plume Number: 9

CUF
Dist: 60 nm

◆ BsGreen
○ PCASP Vd

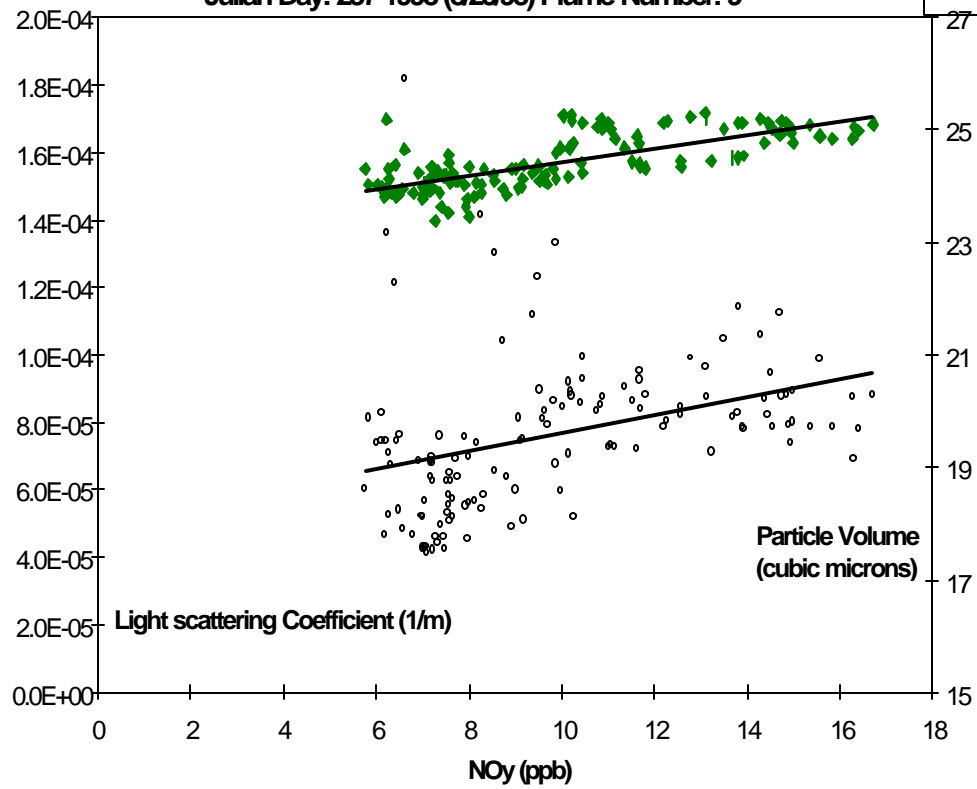


Figure 5.

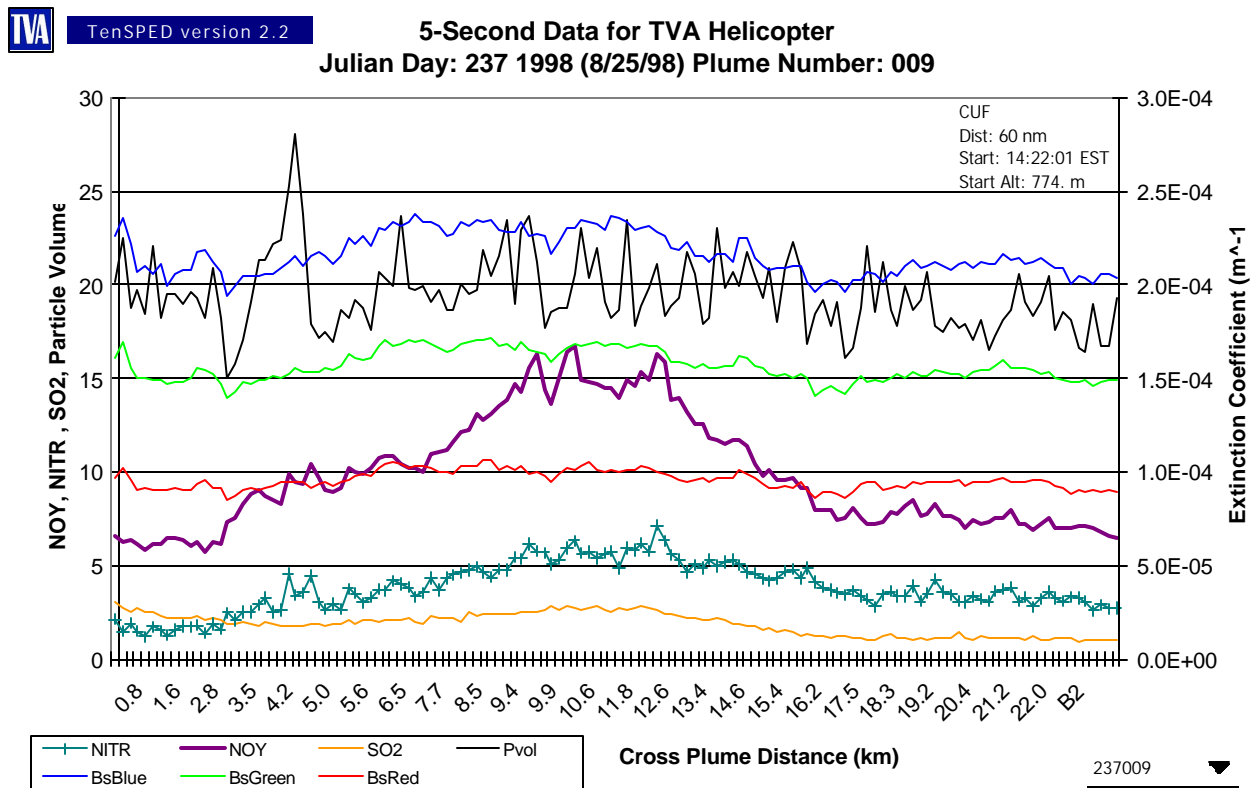


Table 2. Chemical Composition Data for HiVol Samples

Sample No.	Date	Flight No.	Sample Type/ Location	Sampling Vol., m³	[SO₄⁻], mg/m³	[NO₃⁻], mg/m³	[NH₄⁺], mg/m³	Corr. NH₄⁺/SO₄⁻ Molar Ratio
Q98235-BK	08-23-98	6	In-flight bkgd.	32.30	12.59	0.29	2.77	1.137
Q98235-P1			10 nm downwind	13.91	11.32	0.29	2.29	1.038
Q98235-P2			29 nm downwind	15.50	18.23	1.29	3.95	1.045
Q98236-BK	08-24-98	7	In-flight bkgd.	26.12	11.95	0.87	2.53	1.015
Q98236-P1			21 nm downwind	2.52	50.56	3.73	3.73	0.279
Q98236-P2			55 nm downwind	1.99	47.18	5.94	-3.02	-0.536
Q98237-BK	08-25-98	8	In-flight bkgd.	45.53	10.59	0.94	3.51	1.632
Q98237-P1			10 nm downwind	11.60	13.81	2.66	4.33	1.374
Q98237-P2			30 nm downwind	6.83	10.39	3.84	3.63	1.292
Q98237-P3			60 nm downwind	1.09	2.21	31.85	4.97	-10.323
Q98238-BK	08-26-98	9	In-flight bkgd.	23.06	15.59	1.07	4.11	1.300
Q98238-P1			15 nm downwind	5.05	20.17	2.02	5.31	1.249
Q98238-P2			40 nm downwind	8.94	22.78	1.03	4.77	1.046

Plume Ozone Formation and Photochemical Age. There are several new insights that have resulted from examination of the cross-plume traverses from 1998 flights. We are preparing a manuscript based on observations illustrated in Figures 6 and 7 below. Figure 6 shows the plume to be in late stage 2 or early stage 3, with slight wings still showing in the ozone profile, but with ozone concentrations recovered above background even in the middle of the plume. A calculation of the plume chemical age, NO_z/NO_y , (where $\text{NO}_z = \text{NO}_y - \text{NO}_x$), which represents the fraction of emitted NO_x ($\text{NO} + \text{NO}_2$) which has been converted to nitrates and other product species and is plotted with the dashed line in Figure 6, shows some interesting features. The values on the edges of the plumes generally exceed 80%, showing that most of the ozone production capacity of the plume has been exhausted. The values in the center of the plume, where $[\text{NO}_y]$ is still >10 ppbv, are nearly constant at 60-65%, however, and there is only a very narrow region of the plume connecting the edges and the middle with chemical age values in the range of 65 to 85%.

Looking more broadly at the CUF plume at various stages of development, we have developed the frequency plot of chemical age shown in Figure 7. Here we see that even in the fairly fresh plume at 22 km (about $\frac{1}{4}$ of chemical age values $<10\%$), there are still another $\frac{1}{4}$ of values $>80\%$ at the plume edges. This confirms our general hypothesis that the plume is reacting rapidly (at least on warm summer days) at the edges where VOC-rich air is being mixed into the plume. The conversion of NO_x to NO_z continues to occur at the edges until this VOC-rich background air reaches the center of the plume. We are presently examining the previously observed differential loss process for NO_y species with these observations concerning the spatial and temporal pattern of chemical aging in the plume in mind.

One final observation is that we can make these observations concerning ozone productivity, chemical aging and differential loss processes only because we have been able to synchronize the 1-sec data for ozone, all the NO_y species, and for SO_2 to correct for differences in the response times of the instruments prior to averaging the data to its final, 5-sec averaged values.

Figure 6.



TenSPED version 2.2

5-Second Data for TVA Helicopter
Julian Day: 237 1998 (8/25/98) Plume Number: 009

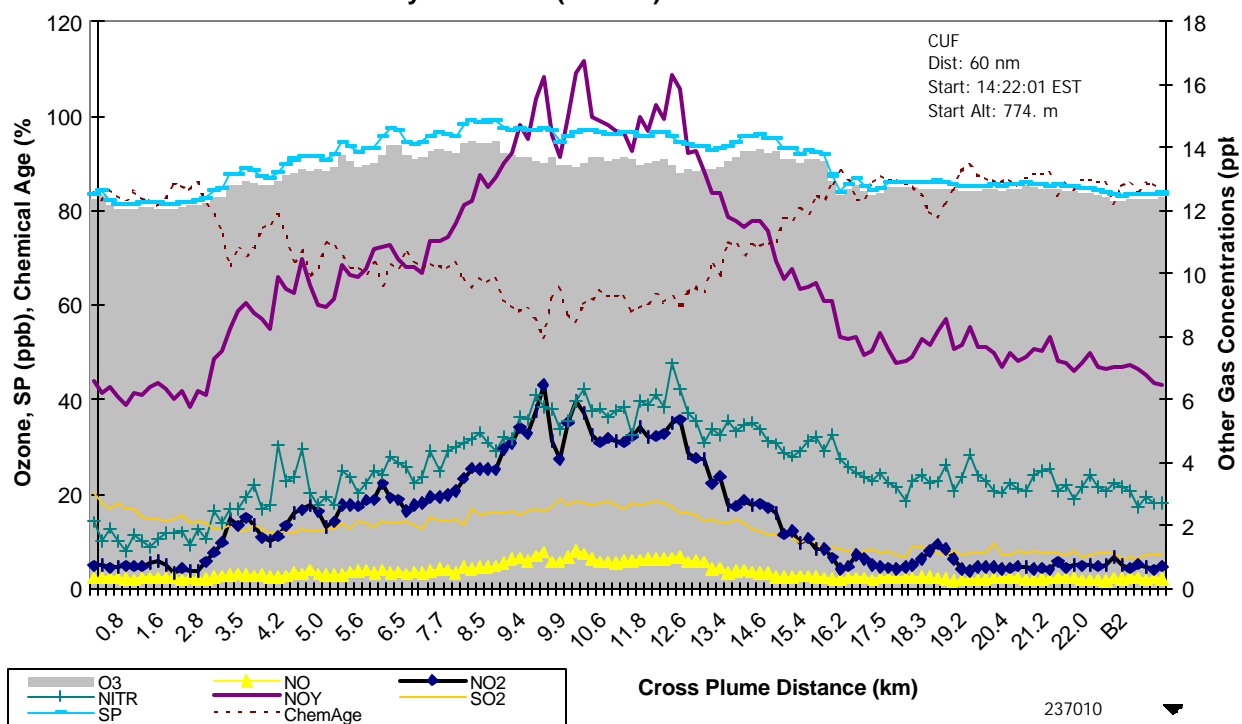


Figure 7.

Plume Chemical Age Profiles

CUF98 8/25/98

Chart Area

